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Ionic Liquids as Potential Cleaning and Restoration Agents for Cellulosic Artefacts

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Abstract: This study explores the efficacy of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide and 1-hexyl-3-methylimidazolium chloride as cleaning agents for aged cellulosic artifacts. A 10% *v*/*v* acetone solution of these ionic liquids (ILs) effectively removes the brownish-yellow color of aged paper in a 10 min immersion treatment. Colorimetric analysis shows a remarkable increase in lightness (L*) by up to 40% and a decrease in red/brownish tones (b*) after IL treatment. The cleaning process also deacidifies the paper, shifting the pH to neutral-slightly basic levels and enhancing its long-term stability. Optimal pH outcomes are achieved, with ionic liquid consumption values of 0.4–0.6 g/g of paper. The FTIR analysis revealed structural changes in cellulose induced by the washing step, which is mainly due to the reorganization effect imparted by the ionic liquids. Furthermore, ILs mobilized degraded compounds and acidic species, aiding in their extraction during the restoration process. Mechanical testing indicated an enhancement in the overall tensile strength and strain at break values for IL-treated papers by up to 33%. This study demonstrates the multiple benefits of alkylimidazolium ionic liquids for preserving and restoring cultural heritage artifacts made of cellulosic materials.

Keywords: ionic liquids; cellulose; paper; restoration; reconditioning agents; cleaning agents

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1. Introduction

The reconditioning and preservation of cultural heritage, both national and international, is a matter of great significance [1,2]. It is essential to acknowledge that a community's future cannot be envisioned without recognizing its past. Among the significant components of humanity's cultural heritage are paper artifacts, which encompass books, manuscripts, leaflets, sketches, drawings, and photographs, among others [3]. However, due to various methods of processing paper supports and the conditions under which artifacts are stored, all paper-based objects are inclined to undergo degradation over time, resulting in a limited lifespan [2].

The degradation of paper artifacts can lead to changes in both their appearance and mechanical properties. Appearance changes may include yellowing, staining, spotting, or fading of colors, which can be caused by (bio)chemical degradation induced by light, humidity, temperature variations, atmospheric oxygen, or degradation of sizers and binders [3–5]. The mechanical properties of paper artifacts can deteriorate due to increased brittleness or tackiness, making them more susceptible to cracking, tearing, and folding damage [3,6]. These changes are influenced by the oxidation and/or hydrolysis of cellulose and by paper acidification, which reduce the degree of polymerization, the crystallinity, and the moisture content of the cellulose fibers under environmental and/or biological factors such as fungi or molds [7].

Considerable research has been conducted in recent decades, leading to the establishment of various standards concerning the restoration and preservation of paper artifacts (such as ANSI/NISO Z39.48-1992) [8,9]. These standards encompass guidelines for maintaining suitable preservation conditions for paper artifacts, including appropriate humidity,

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light, and temperature levels, as well as methods for reconditioning that involve washing, surface treatment, and removal of fungi and molds.

The most common methods used for color restoration of paper artifacts involve either washing or oxidation of the degraded molecules (cellulose, lignin, sizers, binders), which cause paper discoloration [6,10,11]. Washing, oxidation, and deacidification are performed using various solvents and agents, such as water, ethanol, surfactants, supercritical carbon dioxide, hydrogen peroxide, peroxo-containing formulations, chlorine, excimer laser, and alkaline preserves [12–15]. However, these methods have some limitations and drawbacks, such as decreasing the mechanical strength, causing paper warping, and requiring harsh or toxic agents [8,16]. Therefore, there is a need for alternative solvents that can achieve better cleaning and reconditioning results without causing damage to the paper support.

In this work, we propose the use of ionic liquids (ILs) as novel and mild agents for paper cleaning and restoration. The advantages of using these organic salts for paper conservation include their non-toxicity, environmental friendliness, and ability to be tailored to the specific needs of different types of paper and artifacts. By acting as solvents or swelling agents for cellulose, depending on their chemical structure and interaction with the cellulose chains [17,18], ionic liquids (ILs) can overcome some of the limitations of traditional methods. They can affect the cellulose degree of crystallinity, the hydrogen bonding network, and the fibre–fibre bonding of the paper, which are directly responsible for the flexibility of paper and its tensile strength [19].

Ionic liquids can also remove degraded lignin and hemicellulose, which are responsible for the yellowing and staining, from the paper, as well as the acidic species that could promote their deterioration [20,21]. They possess a strong solvation capacity for both small-molecular and macromolecular compounds, including resins, biopolymers, and oils, which are frequently used as binders and sizers for paper artifacts [21]. Additionally, they have proven to be efficient carriers for inorganic compounds such as oxides, silicates, and aluminates commonly used as fillers in paper products [5,18,20]. Compared to water, surfactants, ethanol, or supercritical carbon dioxide, ILs can achieve better cleaning, deacidifying, and reconditioning results without causing brittleness or discoloration [22–24]. Studies conducted on cotton linters, alpha-cellulose, and wood have shown that ILs with 1-alkyl-3-methylimidazolium cation can enhance the resistance of cellulose and lignin to UV degradation, minimizing yellowing and preserving mechanical properties by preventing oxidation [25].

However, it is worth mentioning that the application of ILs in paper-support treatment has been the subject of relatively few studies [20,22–25].

Most of these studies primarily focused on the use of protic ILs, predominantly consisting of alkylammonium cations, as biocidal agents targeting various fungal strains found in specific pigmented areas of damaged books, cellulose substrates, or wood artifacts. Only a limited number of studies have explored the influence of alkylammonium or alkylimidazolium ILs with triazole anions on the optical and mechanical properties of paper, demonstrating promising advancements in reducing yellowing, reducing acidity, and enhancing folding endurance [26–29]. Furthermore, specific ionic liquid formulations based on long alkyl chain compounds with hexafluorophosphate or lactate anions have displayed the capability to increase the repellency of printing paper to water and organic molecules, showcasing their potential in the conservation of paper artifacts [29]. Additionally, ionic liquid-based formulations with enzymes have exhibited promise in effectively removing proteinaceous materials from painted surfaces during restoration treatments [30]. The effectiveness of ILs in removing dirt and grime from paper artifacts, with removal rates ranging from 60% to 100%, has been shown to be higher than that of traditional solvents, which removed 30% to 70% [29–32]. ILs can also offer advantages in terms of time and cost compared with traditional solvents. For example, ILs are able to restore paper artifacts in 24 h, while traditional solvents take several days to a week [27]. Additionally, ionic liquids have the potential to be reused multiple times, making them a cost-effective and sustainable option for paper reconditioning.

The aim of this research is to evaluate the efficacy of two alkylimidazolium ionic liquids, specifically 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIMTs) and 1-hexyl-3-methylimidazolium chloride (HMIMCl), as potential "washing agents" for the reconditioning and conservation of paper artifacts. These ionic liquids possess favorable properties for this application, including a simple structure, liquid state, and compatibility with commonly used solvents, such as alcohols and acetone, which are often employed in restoration processes. Additionally, they can be more accessible in terms of price and batch amounts than the other ILs used in the literature, and they deliver comparable advantages in terms of cleaning but in a shorter time (only 10 min).

An effective paper reconditioning agent should exhibit certain characteristics, such as high penetration ability into the cellulose substrate, minimal or no degradation of the substrate, and no undesirable alterations, such as deposits, warping, or increased susceptibility to physical, chemical, or biological agents. While there are numerous restoration formulations available for paper, none can meet all of these criteria simultaneously. An initial screening performed by our group indicated that 1-hexyl-3-methylimidazolium cations demonstrate lower cellulose disruption ability compared with shorter alkyl chain alkylimidazolium cations while still showing effective solvation properties for smaller molecular or degraded compounds that cause paper staining. Moreover, these particular ionic liquids do not leave waxy deposits, unlike those with alkyl chains exceeding 10 carbon atoms.

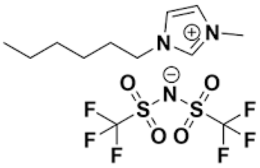
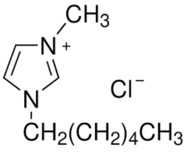
By exploring the advantages offered by these alkylimidazolium ionic liquids in paper treatment, this study aims to provide valuable insights for the scientific and academic communities involved in the preservation of cultural heritage.

2. Materials and Methods

The two ionic liquids used in this study, 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (HMIMTs) and 1-hexyl-3-methylimidazolium chloride (HMIMCl), were obtained from IoLiTec Ionic Liquids Technologies GmbH, Heilbronn, Germany, with a purity of 99%.

Paper strips from an old book were selected to test the ionic liquids (designated as P1, Table 1). The selection criteria included the book's age (published in 1953), a pH of less than 7, and different content values of groundwood and bleached cellulosic pulp.

Table 1. Materials used in the present study and their characteristics (standard deviation values are given in parenthesis).

Paper Type	Book Manufacture Year [1]	pH [2]	Paper Basis Weight	Composition [3]
P1	1953	3.12 (0.20)	63 (0.18) g/m^2	65% (1.16%) groundwood fiber content; 35% (1.23%) bleached chemical pulp, 1.5% (0.26%) ash content
			Ionic liquids type and structure	
			 HMIMTs	 HMIMCl

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[1] as stated on the book's cover page. [2] the pH values of the paper were determined in accordance with Test Method TAPPI/ANSI T 529 om-21 [33]. [3] determined according to [34] (fiber and chemical pulp content) and [35] (ash content), the average of triplicate measurements.

Prior to immersion in the ionic liquids, the paper strips were conditioned for 24 h at 23 °C ± 1 °C and 50 ± 2% relative humidity in a desiccator containing a supersaturated $Mg(NO_3)_2$ solution. The initial weight of the paper strips was measured (m_0).

To prepare the ionic liquid solutions for paper treatment, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-hexyl-3-methylimidazolium chloride were diluted to 10% *v*/*v* using acetone (99.8%, Sigma-Aldrich, Darmstadt, Germany). Acetone was used due to its high evaporation rate, which leaves the substrate dry as fast as possible while delivering the ILs in the structure of the paper.

To assess color and structural alterations, paper strips with dimensions of approximately 20 mm × 60 mm (width × length) were immersed entirely in ionic liquid solutions dissolved in acetone for a duration of 10 min. The choice of this immersion time aimed to minimize any potential adverse effects resulting from prolonged exposure of the paper substrates to the solution. Following removal from the solutions, the strips underwent air-drying under ambient conditions (23 °C) for 24 h. Subsequently, they were conditioned for an additional 24 h at 23 °C ± 1 °C and 50 ± 2% relative humidity before being reweighed (m). This methodological approach ensured a controlled testing environment and minimized the impact of extended solution exposure on the paper samples.

The paper washed with the HMIMCl IL was coded with P1-HMIMCl, while the sample washed with HMIMTs was coded P1-HMIMTs.

Mechanical tests were conducted using strips measuring 10 mm × 100 mm (width × length) following the same treatment protocol.

The specific consumption of ILs (S_{IL}) reported to 1 g of paper (g of IL/g paper) was determined using Equation (1) [29]:

$$S_{IL} = \frac{m - m_0}{m_0} \tag{1}$$

Reference samples (non-treated paper) were conditioned under the same conditions before performing mechanical tests, with at least 10 samples measured for each analysis.

The color modifications of the paper substrates before and after treatment with the ionic liquids were evaluated using a PCEXXM30 colorimeter, which operates in the CIE-L*a*b* color space. In this color space, L* represents the lightness, and a* and b* represent the red/green and yellow/blue coordinates, respectively.

To quantify the total color differences (ΔE^*) for each sample, the following equation (Equation (2)) was used [36]. The subscripts "f" and "i" refer to the values of the color parameters after and before IL treatment, respectively:

$$\Delta E^* = \sqrt{\left(L_f^* - L_i^*\right)^2 + \left(a_f^* - a_i^*\right)^2 + \left(b_f^* - b_i^*\right)^2} \tag{2}$$

All the color measurements were performed on at least three strips of paper per each type of IL treatment, and five measurements were performed on each side of the paper per strip, the average being reported in the paper.

The optical microscopy images were acquired using a Leica DM_ILM microscope at 10× magnification, and the fiber diameter distribution was extracted using image analysis in the dedicated LAS X Materials Science Software version 10 (Leica Microsystems, Wetzlar, Germany). The average roughness (Ra) and kurtosis (Rku) were computed from the optical microscopy images using the GUI to calculate the roughness parameters of images version 1.4.0.0 for MATLAB [37].

ATR-FTIR spectra were acquired using a Perkin-Elmer Spectrum BXII spectrometer (Waltham, MA, USA) in the spectral range of 4000–600 cm^{-1}. Spectra with a resolution of 2 cm^{-1} were obtained, and 32 averaged scans were recorded for each sample.

Tensile tests were performed on the initial and IL-treated paper strips using a Z020 Zwick-Roell (Ulm, Germany) universal testing machine at a testing speed of 5 mm/min. The tensile strength (σ_{br}), elongation at break (ε_f), and Young modulus (E) were extracted from each stress-strain curve. Moreover, the toughness of paper, T (MPa), which represents the amount of energy that the sample can absorb before breaking, was calculated using the instrument's software (testXpert v. 1.1) as the area under the stress-strain curve. The breaking length (BL) of the paper, expressed in meters, is a measure of the inherent strength of the material based on the force required to break a strip of paper that is only self-supporting, was calculated using the following equation (Equation (3)) [38]:

$$\mathrm{BL} = 102000\frac{\mathrm{T}}{\mathrm{R}} \quad (3)$$

where T is the tensile breaking force expressed in kN (taken from the testXpert v.1.11 instrument's software), and R is the paper basis weight (g/m^2).

3. Results and Discussion

The washing step for the old paper cellulosic substrates (P1) by completely immersing paper strips in a 10% v/v acetone solution of the two ILs has proven successful in removing a significant portion of the characteristic brownish-yellow color specific to aged paper (Figure 1), probably due to the high solvation ability of the ILs towards the degraded components in the structure of the material.

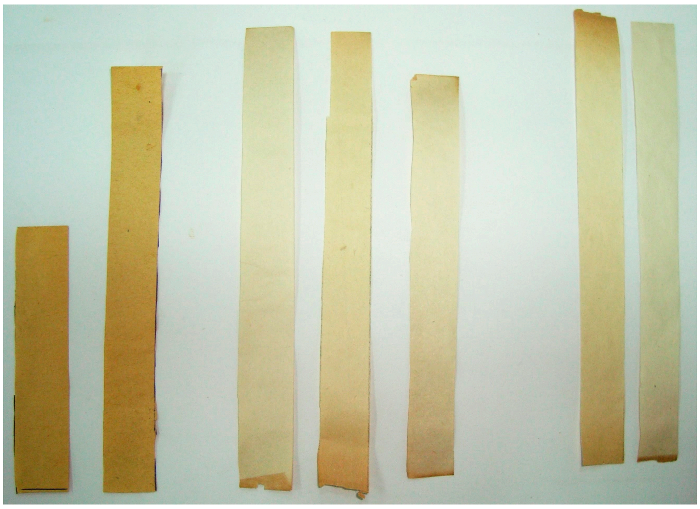
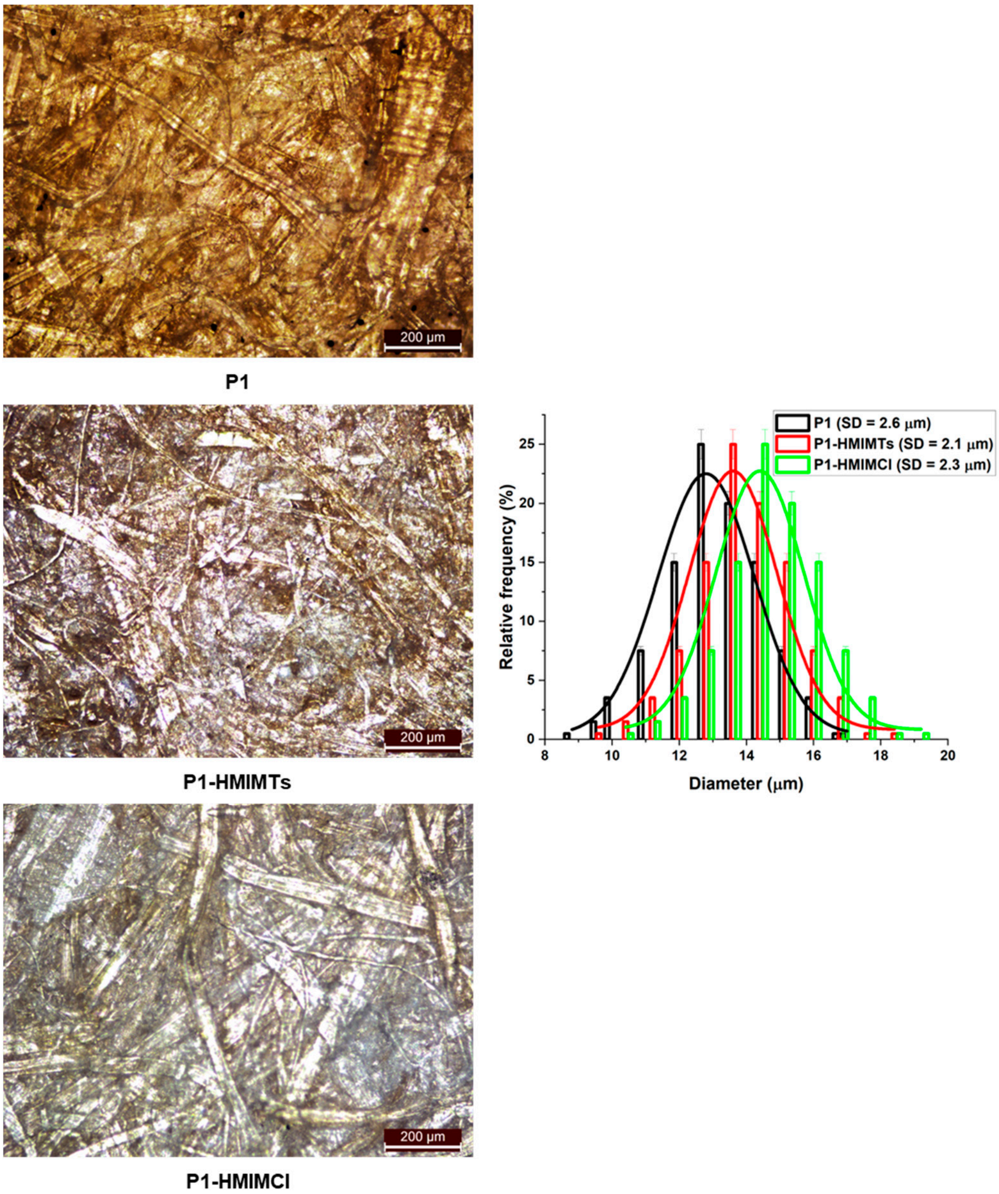


Figure 1. Photographic images of various paper strips used in the washing treatment of P1 old paper substrates.

The paper discoloration is mainly due to the degradation of lignin and hemicellulose, which are components of the paper that form chromophore groups due to reactions induced by light, humidity, temperature, oxygen, and acidic species. The degree and rate of paper discoloration depend on factors such as the type and amount of lignin and hemicellulose in the paper, the presence of other additives or contaminants, and environmental conditions. Ionic liquids penetrate into the paper structure and remove the degraded components, as well as the acidic species that could promote their deterioration. This improves its brightness and whiteness. Figure 2 shows that the P1 sample has the lowest whiteness and the highest grime coverage among the three samples. The paper surface is dark and rough (Ra = 0.87 μm), which indicates a high amount of impurities and binder deterioration. P1-HMIMTS has higher whiteness and cleaner fibers than P1 but slightly lower than HMIMCl. HMIMTs removed most of the degraded components and grime from the paper surface, making it lighter and smoother (Ra = 0.65 μm). The highest degree of smoothness could be due to a combination of fiber swelling and filling air voids with ionic liquid [39]. HMIMCl also smoothed the paper support (Ra = 0.71 μm) and was more effective in removing grime than HMIMTs. The average fiber diameters computed from the optical microscopy images are also presented in Figure 2 and can indicate the interactions of the ILs with paper [40] as well as their cleaning effectiveness. In the three samples, the average fiber diameters (ranging between 12 and 15 µm) increased from P1 to P1-HMIMTs to P1-HMIMCl, which could support the claim that HMIMCl has the highest interaction and cleaning effectiveness. IL treatment also reduces the standard deviation of the fiber diameter for the samples. The mean fiber diameters were within the range mentioned in the reference literature for writing the paper (15–25 µm) [41].



P1

P1-HMIMTs

P1-HMIMCl

Figure 2. Optical microscopy images of various paper strips used in the washing treatment of P1 old paper substrates and the cellulose fiber diameter distributions for each sample.

Regarding the distribution of the fiber diameters, the kurtosis values showed that the surface height distribution is leptokurtic for all samples, meaning that it had a higher peak and heavier tails than a normal distribution [42]. This indicates that the paper surface (Rku = 2.89) had more values near the mean line and near the extremes than a normal distribution.

The ionic liquid treatment reduced the kurtosis of the paper samples Rku for P1-HMIMCl = 2.74), indicating a flatter surface. The P1-HMIMTs sample had the lowest Kurtosis (Rku = 2.54), indicating the most even surface.

The efficacy of the "color restoration" can also be deducted from the colorimetric analysis of the samples (Table 2). The changes in the lightness L parameter on cellulose paper artifacts reconditioning can be attributed to several factors, such as the removal of dirt, grime, and chromophore groups, the swelling of cellulose fibers, and the interaction of ionic liquids with paper components. These factors can affect the optical properties of paper, such as the reflectance, scattering, and absorption of light. Following the application of ILs during the "washing" procedure, there was a notable enhancement in the lightness parameter (L*), which can be associated with the increased whiteness and smoothness of the substrate. This improvement reached up to 40% when compared to the original paper supports. The highest increase in lightness was found for the HMIMCl ionic liquid, which registered the highest cleaning effect and swelling among the cellulose fibers. Similar increases in lightness for ancient color paintings have been explained due to ILs reducing the scattering of light by making the surface smoother and by removing some of the degraded particles that cause scattering [43].

Table 2. The pH, specific IL consumption, color differences, and mechanical properties of the paper samples (average values, with the standard deviation values given in parenthesis).

Sample	pH	S_{IL} (g of IL/g Paper)	CIE-L*a*b* Color Parameters				Mechanical Properties of Paper				
			*L**	*a**	*b**	Δ*E**	BL (m)	σ_{br} (MPa)	ε_f (%)	E (MPa)	T (MPa)
P1	3.12 (0.20)	-	53 (2.83)	4 (0.14)	39 (1.14)	-	16.54 (1.13)	5.11 (0.26)	2.74 (0.32)	67	0.11
P1-HMIMTs	7.70 (0.15)	0.47 (0.08)	79 (2.48)	−2 (0.18)	20 (1.23)	32.75	24.57 (1.25)	7.58 (1.24)	4.05 (0.38)	72	0.19
P1-HMIMCl	7.05 (0.18)	0.61 (0.06)	84 (2.77)	−4 (0.22)	23 (2.12)	35.79	16.32 (1.38)	5.14 (0.93)	4.05 (0.42)	59.42	0.15

The reddish color tones in degraded paper artifacts can be due to the degradation of lignin, hemicellulose, or some organic binders (especially proteins) [44,45]. The reduction of red/brownish tones in the treated supports was evident in the decline of a* values, where positive values indicated red hues and negative values indicated blue hues. The latter can be explained by the removal of degraded components and light scattering by a thin layer of ionic liquid that can remain adsorbed on the surface of the fibers after acetone evaporation. Complexes between ILs and binders can possibly also be formed [46].

Additionally, there was a decrease in yellowness, as deduced from the b* parameter, where positive values signified yellow hues and negative values signified green hues (Table 2). Yellow hues are characteristic of degraded cellulose or other polysaccharide materials that are possibly used as binders in the papermaking industry (starch being the most common) [47–49]. This reduction in a* could signal the removal of the partly degraded cellulose or binder components from the structure of the paper. The ΔE* values showed that the ionic liquid treatment led to significant color differences of the P1-HMIMTs and P1-HMIMCl paper samples compared with P1, indicating a lighter and cleaner material. The P1-HMIMCl sample presented the highest color difference, indicating the most effective cleaning process.

For both P1-HMIMTs and P1-HMIMCl paper samples, the 10% v/v solution of IL compounds used in the treatment exhibits a commendable deacidification capability for paper. This is manifested by a shift in the pH value from neutral to slightly basic levels, which proves beneficial for the long-term stability of paper substrates. The observed pH values are particularly favorable when the ILs are consumed at specific levels ranging between 0.4–0.6 g/g of paper. The specific consumption values, as outlined in Table 1, are either comparable or lower than those reported in other studies. Specifically, they are in line with values documented for various ILs based on 1-butyl-3-methylimidazolium cations, falling within the range of 0.2–3 g/g of paper. Notably, these consumption values are significantly lower than those reported for long-chain didecyldimethylammonium cations, which typically range from 2 to 5 g/g of paper [29].

The mechanism of paper deacidification by ILs can be explained by two main factors: the removal of acidic species and/or their neutralization by the ILs. The removal of acidic species refers to the dissolution or extraction of the degraded components of paper that get oxidized in time to form carboxylate groups ($-COO^{-}$) or other acids that could be formed by sizers hydrolysis (sulfuric acid) or binder degradation (acetic acid) [29,50]. The ILs can penetrate into the paper structure and remove these components. The neutralization by the ILs refers to the reaction of the ILs with the remaining acidic groups in the paper, such as carboxyl groups, that lower the pH of the paper. The ILs with the appropriate structure of the anion or lateral side chains can act as bases and donate hydroxyl ions to the acidic groups. The ILs can also form complexes or coatings on the paper surface, providing a buffer against further acidification [51].

Based on the structure of the ILs used in this study, it is more likely that the mechanism of paper deacidification by the removal of acidic species is the one responsible for increasing pH close to 7 by ILs.

The presence of ILs in the structure of cellulose after washing, as well as the effects of this treatment on the structure of the paper substrate, can be assessed from the FTIR spectra presented in Figures 3 and 4.

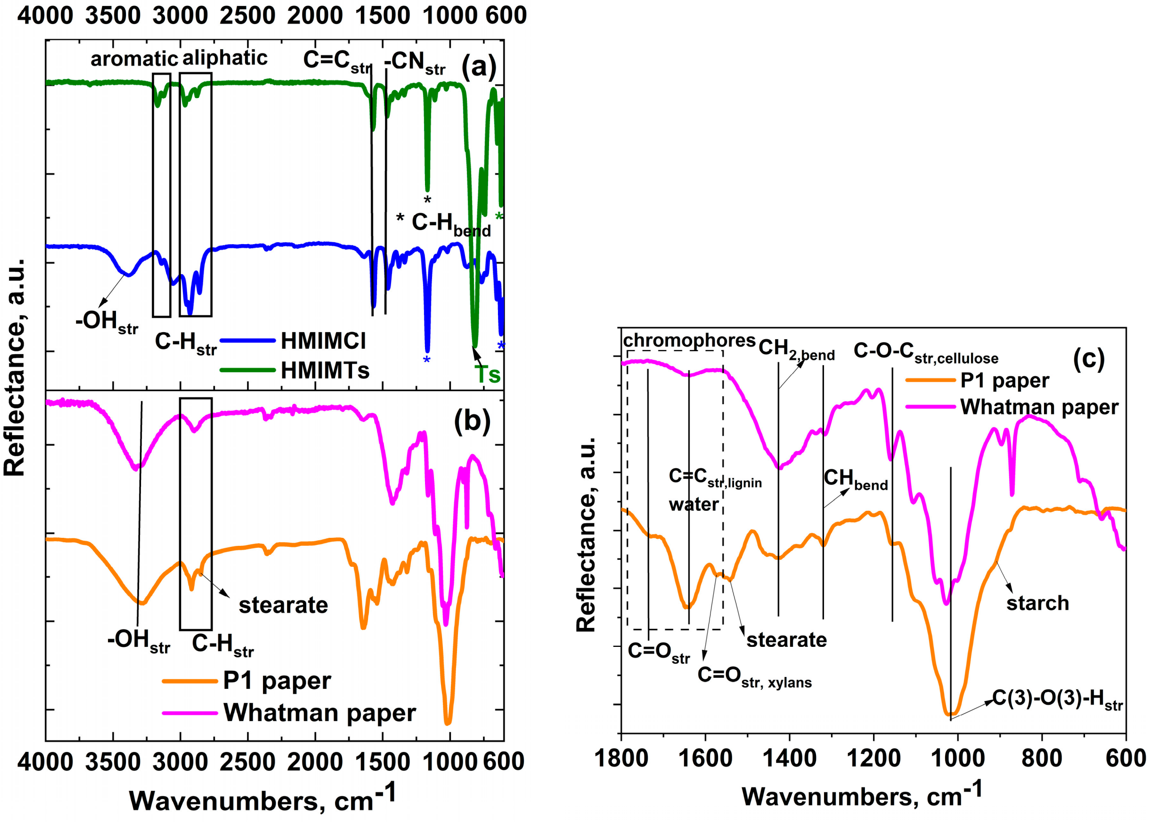


Figure 3. ATR-FTIR spectra of (**a**) ionic liquids used for washing; (**b**) paper substrate and reference Whatman paper; (**c**) detail of the 1800–600 cm^{-1} region for the paper.

The neat 1-hexyl-3-methylimidazolium ILs present distinct structural features, as illustrated in Figure 3a, the most prominent ones being due to the cation (in HMIMCl) or the anion (HMIMTs). Common for both ILs are the absorption bands ascribed to the cation, such as those at 628 cm^{-1}, 1156 cm^{-1} (C–H bending, with overtones), 1473 cm^{-1} (C–N stretch), 1568 cm^{-1} (C=C stretch), and 2883 and 3164 cm^{-1} (aliphatic side chain and aromatic C–H stretching from the imidazolium ring) [52,53]. Additionally, the HMIMCl IL displays a stretching band at approximately 3400 cm^{-1} (–OH stretch vibration), likely attributed to trace amounts of absorbed water in this hygroscopic substance [52]. The bis(trifluoromethylsulfonyl)imide anion exhibits intense bands associated with the torsion of the –C–N–C– bonds at 830 cm^{-1} [53].

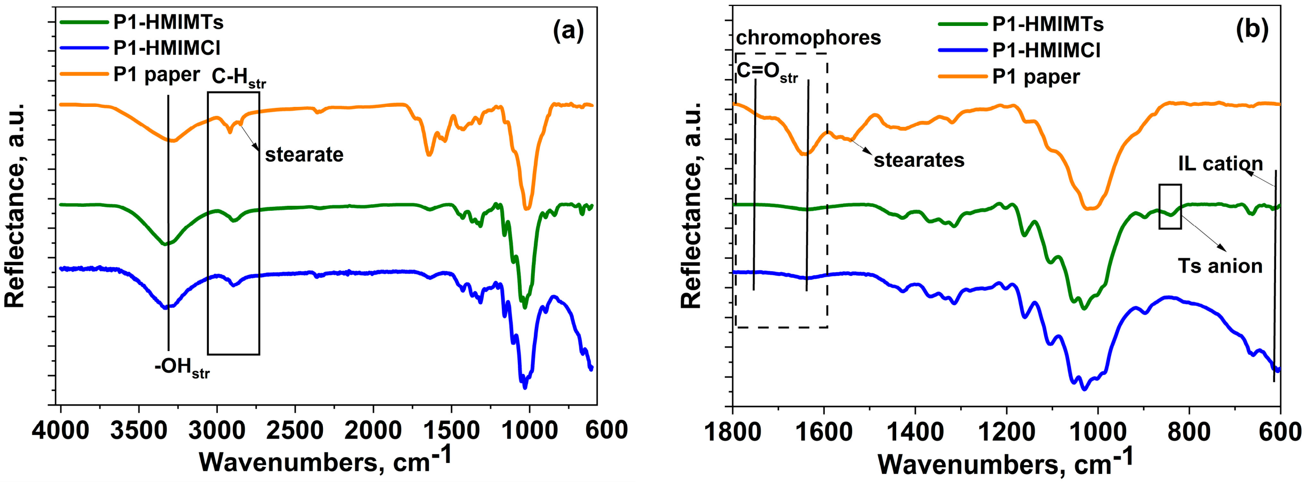


Figure 4. ATR-FTIR spectra of (**a**) IL washed substrates and P1; (**b**) detail of the 1800–600 cm^{-1} region for the washed paper substrates and P1.

Conducting FTIR analysis on paper samples extracted from the old book (P1) and Whatman filter paper (used as a reference and composed of >98% α-cellulose) revealed various bands linked to the primary components of paper, including cellulose, hemicellulose, and paper additives (Figure 3b,c).

Both samples showed strong absorption bands at 3321–3285 cm^{-1} due to hydroxyl groups and at 2898–2910 cm^{-1} due to –CH and –CH$_2$ stretching vibrations (Figure 3b). These bands indicate the presence of cellulose and hemicellulose (in the former) and cellulose, hemicellulose, and lignin (in the latter)—the main structural components of paper [54]. In the fingerprint region of the spectra (Figure 3c), a broad band of 1648–1641 cm^{-1} in both samples was observed, which is likely to be due to –OH bending in weakly adsorbed water. However, for the P1 sample, this band could also be due to C=C stretching in lignin, which makes paper susceptible to degradation [55–57]. Other notable bands that appeared in both spectra were those at 1424 cm^{-1} and 1311–1319 cm^{-1}, ascribed to –CH$_2$ and –CH bending in cellulose and the band of 1162–1161 cm^{-1} due to C–O–C stretching vibration in cellulose and hemicellulose, a polysaccharide that binds cellulose fibers together [57]. The band of 1025–1013 cm^{-1} was also observed in both spectra, which could be due to cellulose or hemicellulose (C(3)–O(3)–H stretching) [58–60].

For the P1 sample, some additional bands were noted that were not present in the reference sample, especially in the chromophore region, where the absorption bands of conjugated double bonds and carbonyl groups are located. These groups are responsible for the characteristic color of old paper and are indicative of the degradation of this material. The band at 1737 cm^{-1} indicated unconjugated C=O and was related to carbonyl groups in hemicellulose, in carboxyl groups belonging to oxidized cellulose (which can be responsible for paper acidification), or to degraded binders [54]. The P1 sample also showed absorption bands that could be indicative of calcium stearate (manifesting as shoulders at 2845 and 1541 cm^{-1}) [61], which is a common paper additive that acts as a lubricant and a water repellent. A shoulder at ~921 cm^{-1} could be associated with starch, another paper additive that improves the surface quality and printability of paper [59,62]. However, its certain identification was difficult due to bands characteristic of binders overlapping with those of cellulose or hemicellulose. The aged paper exhibited weak stretching vibration modes specific to conjugated C=O in xylans from hemicellulose (1582 cm^{-1}) [63,64].

Regarding the semiquantitative assessment of the structural modifications in paper supports, the Hydrogen Bond Index (HBI) was calculated based on the ratio between the intensity of the band at 3321–3285 cm^{-1}, assigned to O–H stretching vibrations and that at 1330 cm^{-1}, specific to the –CH and –CH_2 in-plane bending vibrations. The higher the ratio, the lower the crystallinity, as more hydroxyl groups are available for hydrogen bonding in the amorphous region, which is typical of the conversion of cellulose I (crystalline) to cellulose II (amorphous) [65,66]. The intensities of the bands at 3321–3285 cm^{-1} and 1330 cm^{-1} were the least influenced by the presence of ILs. Other known methods to estimate the crystallinity index for cellulose from IR spectroscopy data make use of the bands at ~2900 cm^{-1} and 1424 cm^{-1}, which are also found in ILs as main peaks or shoulders, respectively [56,60]. Another indicator of cellulose structural reorganization is the asymmetric index a/b, calculated as the ratio between segment widths at half height for the –OH stretching band at 3321–3285 cm^{-1} (calculated from the band maximum) [60].

Generally, higher crystallinity of cellulose is associated with higher strength and stiffness, lower moisture absorption, and lower chemical reactivity of paper. However, the higher crystallinity of cellulose also makes the paper more brittle and less flexible, which can affect its durability and functionality [60,67]. Therefore, there is a trade-off between crystallinity and other properties of paper, depending on the intended use and application of paper.

For the initial material (P1), values of HBI = 3.47 and a/b = 0.99 were obtained in comparison with the Whatman filter paper, which had a HBI = 4.63 and a/b = 1.09. These results suggest that Whatman filter paper may have more amorphous regions of cellulose than writing paper, which could be due to the method of obtaining and purification steps for the cellulose fibers [67]. This could make Whatman filter paper more flexible and absorbent than writing paper but also more susceptible to degradation.

Interpreting the data from FTIR spectroscopy to precisely elucidate the occurrences during the cleaning process of aged paper was challenging, as the spectra showed complex and subtle changes. Nevertheless, it appeared more plausible that alterations in the polymer structure, particularly induced by the washing step and the mobilization of degraded components, played a pivotal role.

One of the most noticeable changes was the –OH stretching band of cellulose, which is sensitive to hydrogen bonds, at around 3330 cm^{-1}. This band became sharper and with lower intensity in the spectra of P1-HMIMTs and P1-HMIMCl compared with P1, which could be correlated with the scission of the intra- and intermolecular hydrogen bonds enacted by the ILs. Moreover, in the case of P1-HMIMTs and P1-HMIMCl, this band shifted to higher wavenumber values (3337 and 3332 cm^{-1}, respectively, compared with 3321 cm^{-1} for P1), implying cellulose reorganization (Figure 4a). This reorganization was supported by the Hydrogen Bond Index (HBI) and the a/b index values, which are ratios of the intensities of different bands related to cellulose structure and hydrogen bonding. The HBI and a/b index values were 3.43 and 1.13 for P1-HMIMTs and 3.52 and 1.16 for P1-HMIMCl, respectively. For HMIMTs, a slight reduction in HBI was observed, which could be explained by the preferential mobilization by the respective IL of a part of the amorphous region, which is more accessible and reactive than the crystalline region [58]. Another change was the disappearance of the alkyl vibration shoulder specific to stearates at 2845 cm^{-1} in the spectra of the washed samples, which was present in the spectrum of P1. This could imply that this compound was also partly mobilized by the ILs.

The ILs removed a significant portion of compounds with chromophore groups, which are responsible for the color and degradation of paper (Figure 4b). The 1737 cm^{-1} broad band found in P1, ascribed to compounds bearing carbonyl and carboxyl groups, disappeared from the spectra of P1-HMIMTs and P1-HMIMCl, indicating an efficient washing of partly degraded hemicelluloses or oxidized species, causing paper acidification [68]. The band at 1648 cm^{-1} ascribed to lignin, a complex polymer that gives paper its yellowish-brown color and makes it susceptible to photochemical degradation, was greatly reduced in intensity in the washed samples and shifted to lower wavenumbers (around 1642 cm^{-1}), which could imply the mobilization of this chromophore compound. The band ascribed to stearates at 1541 cm^{-1} in P1 also disappeared from the spectra of the reconditioned samples.

It is conceivable that a small amount of ILs also persists in the paper, evident through weak absorption bands at ~835 cm^{-1} (Ts anion from bis(trifluoromethylsulfonyl)imide) in P1-HMIMTs and at ~628 cm^{-1} (attributed to the imidazolium cation) in both P1-HMIMCl and P1-HMIMTs. The enduring presence of the ionic liquids (ILs) within the cellulosic material, sustained by the specific consumption values expressed in Table 2, could have some long-term benefits in terms of the biostabilization of paper [26–28] or its interactions with various degradative factors such as variable humidity, exposure to radiation, and more. However, it is important to note that these correlations are subjects of investigation in our forthcoming studies.

According to the TAPPI T 494 om-02 standard, the typical range of the tensile strength, elongation at break, and toughness for writing paper are 40–60 MPa, 2.5–4%, and 0.11–0.14 MPa, respectively [69]. The Young modulus for writing paper is usually between 30 and 50 MPa [38], and its breaking length (BL) is usually between 2000 and 4000 m [38]. However, as shown in Figure 5 and Table 2, the tested samples have much lower tensile strength and breaking length than the standard values, which is expected, given the age of the degraded paper material (~71 years at the time of testing). The elongation at break and toughness are both towards the lower end of the typical range. On the other hand, both IL-washed supports have much higher elongation at break and toughness than the typical paper and paperboard types. This suggests that the samples are more flexible (the Young modulus presents lower or similar values compared with P1) and resilient but still less resistant to breaking than a new paper.

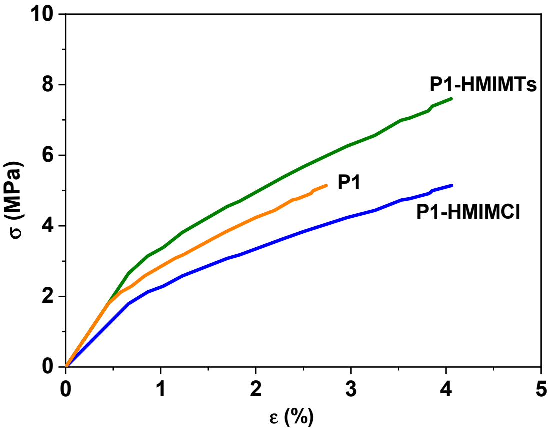


Figure 5. Stress-strain curves for P1 paper and IL-treated paper.

Results indicate that the IL treatment improves the tensile properties of the reconditioned samples up to 30% compared with P1, especially the HMIMTs treatment, which shows the highest increase in tensile strength, elongation at break (with 33%), and toughness (with up to 73%). This implies that the ILs can penetrate the cellulose fibers and restructure the hydrogen bond network, enhancing their cohesion and elasticity. HMIMCl also causes some reduction in cellulose crystallinity, which lowers the fiber's stiffness (the Young modulus of P1-HMIMCl). Cellulose/binder plasticization by ionic liquids can be a possible mechanism to explain the improvement of the mechanical properties of the reconditioned paper. Some studies have reported that ILs can lower the T_g of cellulose and cellulose derivatives, such as cellulose acetate and cellulose triacetate, by up to 100 °C [70]. This indicates that ILs can increase the mobility and deformability of the cellulose chains, resulting in higher elongation at break and toughness of the reconditioned paper. The FTIR spectroscopy data sustain extensive reorganization of the secondary bonds in the paper support.

Regarding paper supports reconditioning, other methods of consolidation, such as with cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs), and nano-SiO_2 materials, can increase the toughness of paper by 100% compared with the original paper. However, the nanomaterials also increase the density and decrease the porosity of paper, which may affect its breathability and flexibility [71,72]. Enzymatic treatment can improve the tensile strength, elongation at break, and toughness of the reconditioned paper by up to 50% compared with the original paper. However, the enzymes also cause an increase in the hydrophilicity and porosity, as well as some hydrolysis and oxidation of the cellulose chains, reducing their degree of polymerization and crystallinity [72].

Further research and exploration of the advantages offered by alkylimidazolium ionic liquids in paper treatment can contribute to the preservation of cultural heritage.

4. Conclusions

Alkylimidazolium ionic liquids, specifically 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-hexyl-3-methylimidazolium chloride, showed promising results in terms of color restoration, cleaning effectiveness, deacidification, and mechanical property enhancement in the restoration of aged cellulose paper substrates. Both ionic liquids demonstrated effectiveness in reducing paper discoloration, enhancing whiteness, and improving surface cleanliness, with the one with chloride anion marginally proving more efficient.

Both ILs, when used at specific levels (0.4–0.6 g/g of paper), exhibited commendable deacidification capabilities, shifting the pH from neutral to slightly basic levels. The observed pH values were favorable for the long-term stability of paper substrates, and specific IL consumption levels were comparable to or lower than values reported in other studies.

IL-treated samples showed improved tensile properties compared with untreated paper, suggesting enhanced flexibility, toughness, and resilience.

This study demonstrated the potential of ionic liquids as mild cleaning and restoration agents, as they eliminate the need for oxidation agents that could cause degradation and harm to the paper support. However, further studies are needed to evaluate other aspects of ionic liquids in paper restoration, such as their effects on UV resistance, biodegradability, and toxicity of the paper. Moreover, their long-term impact on more types of paper, from different time periods and with different compositions, is needed.

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